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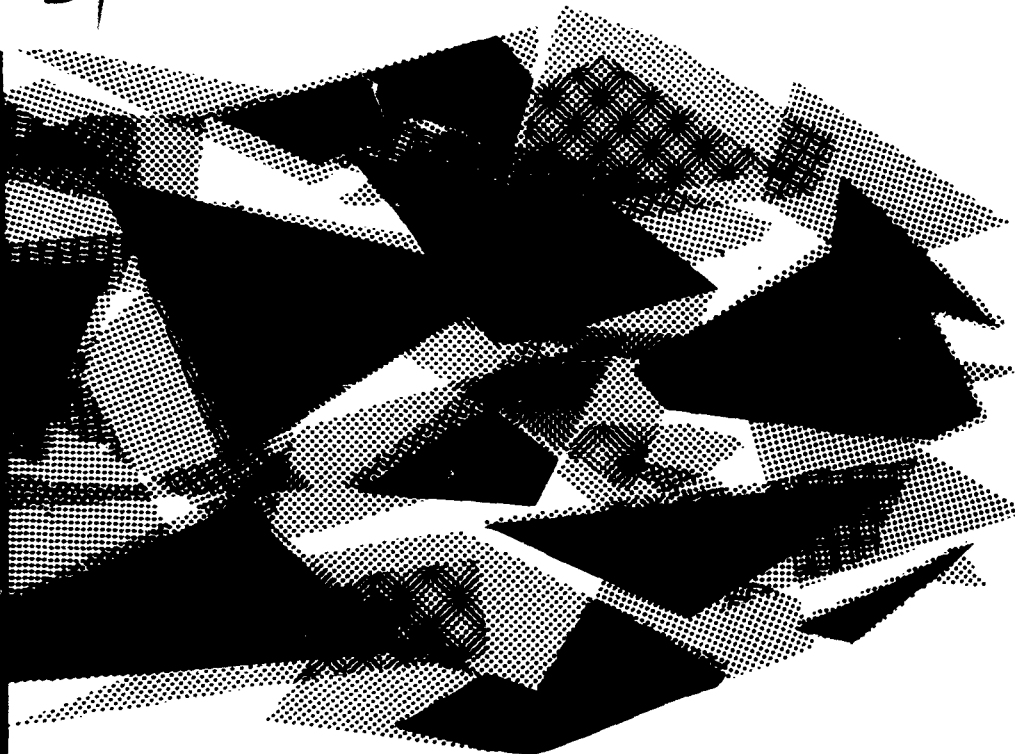
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COMBUSTION OF SOLID PROPELLANTS
AT HIGH PRESSURES—A SURVEY (U)

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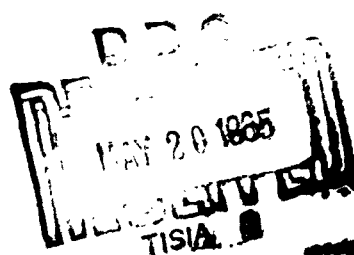
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Report No. S-71

COMBUSTION OF SOLID PROPELLANTS AT HIGH PRESSURES—A SURVEY

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May 20, 1965

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C O N F I D E N T I A L

ROHM & HAAS COMPANY

**REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA**

**COMBUSTION OF SOLID PROPELLANTS AT HIGH
PRESSURES—A SURVEY**

ABSTRACT

The classified literature dealing with deflagration characteristics of solid propellants at pressures exceeding 2000 psia has been screened. References from 1947 through 1964 on pure oxidizers and inert-binder composite propellants have been assembled into an annotated bibliography.

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COMBUSTION OF SOLID PROPELLANTS AT HIGH PRESSURES—A SURVEY

INTRODUCTION

Coincident with the increasing importance of high chamber pressures in solid rocket propulsion, a need has developed for a comprehensive survey of the literature on high pressure solid propellant (heterogeneous and homogeneous) combustion. This report is the first of a projected series dealing with this subject and is aimed at (1) gathering high pressure composite propellant and pure oxidizer combustion data in a single location, and (2) evaluating these data.

The literature reviewed in the course of this study was that abstracted by the Chemical Propulsion Information Agency (and its predecessor the Solid Propellant Information Agency) from August 1947 to December 1964, inclusive (SPIA Volumes A/1 through A/22; CPIA Volumes CPA/63 and CPA/64). Abstract subject headings searched included: "Ammonium Perchlorate"; "Ballistics, Interior"; "Bombs"; "Burning"; "Burning Rate"; "Combustion"; "Detonation"; "Explosives"; "Grains"; "Gun Propellants"; "Oxidizer"; "Pressure"; "Propellants"; "Propulsion Systems"; "Rocket Motors"; "Rocket Propellants—Solid" and similar headings with titles varying among the various volumes reviewed. Only those references whose abstracts indicated particular concern with combustion pressures appreciably exceeding 2000 psi were considered further.

Of the references obtained from this source (about sixty), forty deal with intermediate-pressure combustion studies (at pressures exceeding 3000 psi) and thirty with work involving high pressures (above 5000 psi). In the latter group, the majority of references (about twenty) deal with closed bomb tests to pressures above 20,000 psi; the results reported may be of doubtful accuracy at pressures below 10,000 psi.

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Intermediate- and high-pressure data come largely from Hercules Powder Company, Allegany Ballistics Laboratory; Aerojet-General Corporation; U. S. Bureau of Mines; U. S. Naval Ordnance Test Station; Picatinny Arsenal; and this Division of Rohm & Haas Company. They deal for the most part with double-base and composite-modified double-base propellants. However, a number of references to intermediate combustion pressure studies with the so-called "inert-binder" composite solid propellants were found.¹ Several references regarding high pressure combustion of pure ammonium perchlorate have been located and some work on pure ammonium nitrate has been mentioned.

While it was originally thought that Chemical Abstracts would provide additional useful references, a check of four years' volumes of this publication (1958- 1961, inclusive) produced pertinent references which only duplicated some of those already obtained from CPIA abstracts. Hence, Chemical Abstracts was not reviewed further.

A solid propellant bibliography covering the period 1859 to 1956 was also consulted.² Its references on high pressure combustion deal for the most part with closed bomb experiments on double-base propellants.

The references located probably do not constitute a comprehensive survey of high pressure combustion data. In several instances, e. g., (001) (011) (103) (104),³ additional data not referenced in the abstracts searched has been included, but it is likely, particularly in the case of ammonium nitrate and propellants based on it, that appreciable omissions still exist. The effort involved in a truly comprehensive survey of this field was unjustifiable within the desired scope.

¹The term "inert-binder" is used throughout this report simply as a convenient designation for binder materials which do not contain an oxidizing moiety.

²A. J. Zaehring, "Solid Propellant Bibliography," Jet Propulsion, 27, 900-927 (1957).

³Numbers in parentheses indicate references in the Annotated References which is divided into two groups, Series 000 containing references for Part I (Oxidizers) and Series 100 containing references for Part II (Inert-Binder Composite Propellants).

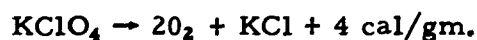
High pressure burning rate data for propellants with binders of polysulfide (PS)¹, polyurethane (PU), polybutadiene-acrylic acid (PBAA), carboxy-terminated polybutadiene (CPB), polyester-acrylic (PE), asphalt (A), and asphalt-oil (A-O), with oxidizers such as ammonium perchlorate (AP), potassium perchlorate (KP), and RDX, and with additives of ferrocene (F), copper chromite (CC), and aluminum (Al) have been reported. Pure AP burning rate data have also been reported. These data are collected and reproduced in Figs. 1 to 8,² with some superimposed r-P data for pressed AP strands shown in Figs. 1 and 4 through 8 for comparison among similar figures. The data are largely from strand burner experiments (as indicated in the figures), using fuse-wire time-interval determinations.

In general the curves shown reproduce data curves as they appear in the various references. No attempt has been made to smooth those data originally reported graphically as intersecting straight-line segments. Data for combustion pressures below 1000 psia have not been shown. Published data from Aerojet-General for pressed strands of AP-KP and AP-KCl mixtures (115) and pure AN (004) have not been shown since the scatter of these data is too great to draw significance and conclusions from them.

I. OXIDIZERS

Potassium Perchlorate

No data were found involving the deflagration of pure or catalyzed potassium perchlorate. This is not surprising as it is doubtful whether the mildly exothermic potassium perchlorate decomposition³



will support deflagration.

¹A key to the composition coding used in the figures and in the Annotated references appears in Table I.

²The points indicated in Figs. 2 through 8 are shown merely for curve identification. In general, the data presented should be interpreted only with cognizance of the comments in the Annotated References, since oxidizer particle size, strand burner type, etc., cannot be disregarded as possible factor

³R. D. Geckler, "The Mechanism of Combustion of Solid Propellants"; Selected Combustion Problems—Fundamentals and Aeronautical Applications (AGARD), Butterworths (1954), p. 325.

Table IPropellant Composition Key**Fuels:**

PS	=	polysulfide
PU	=	polyurethane (including nitroplasticized)
PBAA	=	poly(butadiene acrylic acid) copolymer
CPB	=	carboxy-terminated polybutadiene
PE	=	polyester-acrylic
A	=	asphalt
A-O	=	asphalt-oil
PVC	=	poly(vinyl chloride)

Oxidizers:

AP	=	ammonium perchlorate
KP	=	potassium perchlorate
AN	=	ammonium nitrate

Additives

Al	=	aluminum
KCl	=	potassium chloride
CC	=	copper chromite, usually CuO ₂ O ₂ (Harshaw)
F	=	ferrocene
CB	=	carbon black

Ammonium Perchlorate

It is evident from the various data reviewed that in the region between about 2000 and 10,000 psia there is an appreciable dependence of burning rate upon sample size, restrictor, and possibly the original AP particle size before pressing (Figs. 2 and 3).

There are two aspects of this apparent burning rate sensitivity. First, in a variety of strand sizes and shapes, there is a strong tendency toward depression of burning rates in this pressure regime and, if strands are completely unrestricted, toward eventual cessation of burning before complete consumption of the strand. Attempts to eliminate this tendency at Atlantic Research Corporation (009), Aerojet-General Corporation (003) and by Russian workers (011) through restriction of strand sides or shielding of the burning surface by strand wrapping have met with varying success, depending on the details of the techniques and materials used. Rates depressed below "normal" may be attributed to strand effects through convective heat loss (009).

The second aspect of AP burning rate sensitivity in the 2000 to 10,000 psi pressure regime is the trend toward high burning rate pressure index or "transition" at high pressures. This trend is evident in data from two independent sources—Aerojet (003) and the Russian literature (011). It has been attributed by Aerojet to microscopic fracture of pressed crystalline AP acted upon by the thermal stresses induced by the solid-phase temperature gradients inherent in the deflagration wave (004). No published attempt is known aimed at reconciling this mechanistic view with the Russian data (011). For example these data show (Fig. 3) that, for 7-mm strands, the tendency to high burning rate pressure index apparently can overbalance the previously mentioned trend toward depressed rates in unrestricted and unshielded strands.

In contrast to the data obtained by Aerojet (003), the more recent Russian data (011) suggest that it is inappropriate to speak of a single r - P curve for pure AP at pressures above transition. Since these recent data have not been discussed in the English-language literature, the implication is that they are not widely known or that they have not been given serious consideration. Whatever the reason for overlooking the Russian work the result has been that the significance of the earlier r - P data of Aerojet has been extended to a variety of deflagration situations quite different from the specific sample and test configuration for which these data were taken.¹ The Aerojet data do, however, represent the highest rates yet observed for pure AP burning at pressures beyond transition. Whether this fact is indicative of an independence of the Aerojet data from the strand and restrictor influences found by the Russian investigators is uncertain, but a priori conclusions in this direction are certainly unsubstantiated. The variations of AP burning rates above transition by almost a factor of three, depending on sample preparation (see Fig. 2), must be accounted for in any attempt at mechanistic description of the transition phenomenon.

Though r - P data for catalyzed AP strands have been reported by Atlantic Research Corp. workers (005) (007), these data have not been reproduced in this survey since they are of doubtful significance. These are the only catalyzed AP data known but they were obtained from measurements on unrestricted, unshielded strands; this configuration was found later by the same workers to give anomalous results, reportedly due to convective heat loss (009).

Ammonium Nitrate

With the exception of the scattered data of Aerojet (004), no high-pressure combustion data for either ammonium nitrate or ammonium nitrate-oxidized inert-binder propellants was found in the course of this survey.

¹See discussion of the Thiokol-postulated upper pressure limit in the section entitled "Propellants Containing Ammonium Perchlorate."

II. INERT-BINDER COMPOSITE PROPELLANTS

The collected high pressure combustion data for inert-binder composite propellants may conveniently be divided into three classes on the basis of r - P trends: propellants containing potassium perchlorate, those containing ammonium perchlorate, and those containing RDX.

Propellants Containing Potassium Perchlorate

High-pressure burning rate data for KP-containing inert-binder composite propellants (Fig. 4) may be extrapolated from low-pressure (below 1000 psia) data. A high burning rate pressure index ($n = 0.7$ to 1.0) characteristic of KP-oxidized propellants at lower pressures is still in evidence at higher pressures (20,000 to 50,000 psi); it shows no abrupt changes within the broad pressure-burning rate-composition regime tested.

Propellants Containing Ammonium Perchlorate

Extensive data were found in the literature regarding the high pressure combustion of AP-containing inert-binder composite propellants (Figs. 5 to 7). However, few of these data appear to represent systematic attempts to single out the various possible influences on high-pressure r - P relations. Hence, only broad conclusions can be reached in considering these data.

For the purpose of discussion, it is useful to view two aspects of high-pressure r - P data. The first aspect is that of the pressure index, n , of the propellant burning rate in the familiar empirical relation $r = aP^n$. This index shows a strong tendency toward high values ($n > 1$) at high combustion pressures. The second aspect is that of the magnitudes of high-pressure burning rates and, hence, the extent to which pressure affects the order and range of burning rates for different propellants. This dual approach to the analysis of r - P data is ballistically and mechanistically oriented, and to a certain extent complicates discussion. Burning rate

magnitudes and pressure index are truly separable mathematically only when the index is independent of pressure, i. e., $n = \frac{\partial \ln r}{\partial P} = \text{constant}$. Nonetheless, the classic analysis of r-P data via separate burning rate magnitude and pressure index specifications is useful enough to warrant this approach.

Pressure Index - The most notable trend observable in high-pressure r-P data for inert-binder propellants with AP oxidizer is that toward a high pressure index. All available data for common AP propellants (Figs. 5 to 8) show that an index exceeding unity is reached at some pressure and burning rate (typically, between 4000 and 10,000 psi and 0.4 to 1 in/sec). With the exception of the data for two of the polysulfide AP propellants reported by workers at Princeton (109), all data for AP-containing propellants exhibit maximum indexes near 1.75. The Princeton data show maximum indexes of about 1.25.

It is extremely interesting that almost all propellants appear to reach a maximum value of n very near that exhibited by the r-P data for pure AP reported by Aerojet (003) and in the Russian literature (011). Of further interest is that, without exception, all attain values of n appreciably above unity at pressures and burning rates near that of the transition of pure AP. These observations strongly suggest an influence of AP deflagration and its mechanism on AP-propellant burning rates at high pressures. Such a suggestion was made (007), in fact, well before transition phenomena in AP were first reported by Aerojet (003) and before the similarity between AP and AP-propellant transition was observed. This similarity serves to substantiate further the prime importance of the constituent common to these propellants and which distinguishes them from propellants which do not exhibit transition, viz., AP oxidizer.

For pressures above that at which a maximum pressure index is attained, workers at Princeton (109) have reported several r-P curves for polysulfide-AP propellants (Fig. 5) which exhibit a further interesting

effect, i. e., an eventual decrease in pressure index at the 15,000-20,000 psi level. The large number of data points reported for these curves substantiate the trend, but the possibility of modification by other factors—test configuration, propellant binder type, etc.—cannot be eliminated since all these data are from one laboratory, for a single sample size and burner design, and for a narrow range of propellant compositions. If these data are valid, they are especially interesting. Such a trend to an eventual post-transition decrease in n is reported to occur in only one of five high-pressure r - P curves for pure AP. Hence, it is possible that an eventual decrease in propellant indexes at pressures above transition involves modification of high-pressure propellant burning by some factor or mechanism absent in the burning of pure AP.

While the maximum index achieved in the combustion pressure regime between 4000 and 10,000 psi has typically been reported to be of the same order as that for pure AP burning in this regime, there is a notable exception in the cases of high burning rate propellants ($r_{1000} > 1$ in/sec). Several catalyzed and aluminized formulations (polybutadiene-AP) have exhibited neither high values of n nor trends toward such at pressures below 15 kpsi, the maximum pressure at which they were tested, i. e., transition has not been observed.¹ The absence of such a trend is also seen to be the case with polyvinyl ethyl ether-AP propellant and a catalyzed polyester-AP propellant both of which display intermediate-level burning rates (1.0 to 1.5 in/sec at 2000 psi) (Fig. 6). Thus, it is clear that influences other than merely the presence of AP play important parts in determining high pressure r - P relations. One of these may be the cause of the trend toward an eventual decrease in n at high pressure discussed above. Unfortunately, the incompleteness of presently available r - P data between 4000 and 10,000 psi precludes characterization of these influences in terms of normal propellant variables—binder type, AP particle size distribution and loading density, catalyst

¹David Flanagan, Thiokol Chemical Corp., Huntsville Division, private communication, Dec. 5, 1964.

content, metal additive content, etc. The relative importance of these influences, however, is at least suggested by the different shapes (abruptness of transition) of the various r - P curves available, despite their nearly common maximum indexes (slopes) once transition has occurred.

While exhibiting strong tendencies to values of n which increase with pressure, the shapes of the various r - P curves differ appreciably in the magnitude of the pressure ranges over which this tendency is evident. The shapes also vary within each range. This dependency of the r - P curve shape on propellant variables is to be expected, since transition to a nearly constant maximum n from low-pressure values of n which are functions of other characteristics such as binder type should be similarly dependent. For a given propellant type, there is evidence that either the burning rate level itself or the variables influencing burning rate may affect the r - P curve shape in the transition region, though possibly not the maximum slope. Thus, while there is appreciable evidence that many AP propellants attain at high pressures a pressure index very near that of pure AP, the transition process at pressures below that corresponding to the maximum index seems to depend on other details of propellant composition. This point will be treated further in the following discussion of the second aspect of transition, i. e., burning rate level or magnitude.

Burning Rate Magnitudes - It is worthwhile to consider, in addition to pressure index, the interplay between absolute burning rate levels and transition phenomena. Caution is in order, however, since it is easy to be misled by an illusory trend toward convergence of r - P curves or burning rate levels (Fig. 1) for different propellants during transition to a high index. This apparent convergence must be interpreted cautiously since, as is easily verified, two r - P curves of varying slopes on log-log coordinates will typically appear more nearly congruent the greater their slopes are, even though a constant ratio of actual rates at a given pressure is maintained.

The envelope of high pressure r-P curves which exhibit transition and which cover the range of 1 to 10 kpsi (Fig. 9) actually does not vary in height (burning rate range at constant P) by more than about 18%, being broadest at a mid-range pressure. While the envelope appears to narrow at high pressures, the envelope boundaries at the extremes of pressure (7 and 10 kpsi) differ only by about 6%. The data considered, therefore, do not conclusively demonstrate a trend toward substantial narrowing of the r-P curve envelope at high combustion pressures if only those propellants undergoing transition are considered. If high burning rate propellants which do not indicate transition are additionally considered, then a pronounced tendency toward burning rate convergence is apparent, but the significance of such a convergence is uncertain.

Selected r-P curves for a given binder type do indicate convergence in some cases where transition occurs (Figs. 5 and 6), while in other cases they do not (Fig. 6). The data available are not extensive enough to justify firm conclusions regarding such convergence.

Some of Thiokol's unpublished data and r-P curves (not reproduced in this report) are notable with regard to the apparent convergence of r-P curves for AP propellant systems of a fixed binder type.¹ Thiokol investigators have obtained data for polybutadiene-AP propellants which show partial r-P convergence and pressure indexes near 1.75 at pressure above transition (ca. 10,000 psi). The propellants contained a variety of oxidizer particle size distributions, some contained catalysts, and some had aluminum. The reported r-P curves displayed near-congruity above transition with Aerojet's pure-AP, post-transition r-P curve. This has led the Thiokol investigators to suggest the Aerojet

¹David Flanagan, Thiokol Chemical Corp., Huntsville Division, private communication, Dec. 5, 1964.

r-P curve as a possible approximate high-pressure boundary in the r-P plane of normal low-index combustion of AP-oxidized propellants; this boundary is followed by AP propellant r-P curves after intersection with it. The concept of the pure AP burning rate curve as a boundary of normal, low index burning may explain why high burning rate propellants have not displayed transitions, i. e. some low pressure, low index r-P curves with high burning rate magnitudes do not intersect the pure AP burning rate curve at pressures low enough to fall within the r-P regime tested to date. The failure of high burning rate propellants to display transition may, however, also be related to the phenomena involved in the reported trends of some propellants to undergo a post-transition decrease in pressure index as mentioned above.

Summary - In summary, inert-binder solid propellants containing AP typically exhibit transition to pressure indexes exceeding unity at pressures between 4000 and 10,000 psi. The pressure range and shape (on r-P coordinates) of this transition depends on burning rate level or on the compositional factors controlling burning rates or both. There is conjecture that an important aspect of this burning rate level dependence is the point of intersection of a propellant's low-pressure r-P curve and the Aerojet r-P curve for pure AP (above transition). Hence, high burning rate propellants may not exhibit transition in the usual pressure range (say, $P < 20,000$ psi).

Further, there is some evidence that, for a given binder type, the influences of oxidizer particle size distribution and catalyst content diminish appreciably during transition. This would explain an observed tendency of r-P curves for propellants of a given binder type to converge at high pressures. Differences in fuel binder type, however, appear to affect r-P relations both during and after transition. This effect has the result that the envelope of any set of propellant r-P curves for different binders, while displaying a high index, does not appear to narrow appreciably on log-log coordinates. In general, however, presently available r-P data for AP propellants burning at high pressures are too scant to allow well-substantiated

conclusions regarding the effects of typical propellant variables such as oxidizer particle size distribution and loading fraction, metal and catalyst content, flame temperature, etc.

Propellants Containing RDX

The only data which have been located for propellants containing RDX are those for two PU-AP-RDX-Al formulations of Aerojet (120-122). The r-P trends for these propellants (Fig. 8) are quite different from those for propellants without RDX. The data are notable in that there are no abrupt transitions observable,¹ that high indexes ($n \geq 1$) with a slight tendency to increase are observed through the whole pressure range, and that an AP particle size effect on rate may be more apparent at high pressures than at low.

Interesting in comparison with the Aerojet propellant data are those data reported from two sources, Aerojet (123) and Rohm & Haas (124, 125) for RDX with small percentages of inert binder (Fig. 8). The Aerojet data for 3% polystyrene-RDX mixture burning between 200 and 1500 psi show a low index (0.46), and relatively high rates ($r_{1000} = 0.73$ in/sec). In contrast, the Rohm & Haas data for 2% polyvinyl ethyl ether-RDX (600 to 20,000 psi) and pure RDX (1000 to 3000 psi) show higher indexes ($n = 0.70$ to 1.0) and lower rates ($r_{1000} = 0.1$ to 0.45 in/sec) than that of Aerojet.

Of further interest is that pure RDX has been reported in the Russian literature to burn with a pressure index of unity at pressures to above 10,000 psi² but the data referred to were not located in the references cited by Andreev.

The reasons for the differences in both indexes and rates among the Aerojet, Rohm & Haas, and Russian results for pure and near-pure RDX are not clear, but quite possibly involve details of sample

¹The short, very-high-index portion of the upper curve in Fig. 8 is attributable to experimental scatter shown by the original data.

²K. K. Andreev, "Physical Thermal Stability of Crystals of Some Explosives," Nauchn. Dokl. Vysshei Shkoly, Khim. i Khim. Tekhnol. 1959 (2), 244-6 (in Russian).

preparation, test conditions, etc. Further experiments are required to clarify these effects.

Discounting these apparent discrepancies in RDX burning rate data, it is still apparent that the presence of RDX in propellants may dominate r - P relations even though the propellants contain appreciable quantities of AP. The details of the interplay between different rate- and index-determining effects in propellants containing RDX must, however, await further experimentation.

ANNOTATED REFERENCES

Series 000—Oxidizers

- 001 D. J. Sibbett, and J. M. Lobato, "Investigation of the Mechanism of Combustion of Composite Solid Propellants," Aerojet-General Corp., Final Report No. 1782, 38 pp. (April 1960).

Fuse wire and photographic measurements of pure-AP burning rates at pressures between 1 atm. and 1400 psi. with unrestricted and Acryloid-restricted strands of variable size and geometry (unspecified), under conditions including venting of combustion products and nitrogen purge flow and in closed chamber situations using an end-to-end, two-strand configuration. Considerable scatter (lying mostly above the plotted r-P curve) of up to 100% in burning rate. Flattened thermocouples between the end-to-end strands provided temperature profiles; peak temperatures up to 1200°C at 500 psi. Complete combustion of the samples was obtained at pressures as low as 320 psig. Contrary to Ref. 009, ignition was achieved at very low sample temperatures (-196°C). Gas phase reactions were studied, including ammonia-perchloric acid and perchloric acid thermal decomposition. Vapor pressure and IR spectral data for perchloric acid are reported.

- 002 W. H. Andersen and O. R. Irwin, "Susceptibility of Solid-Composite Propellants to Explosion or Detonation," Aerojet-General Corp. No. L0253-02-2, 15 pp. (June 7, 1960) (Confidential).

Published data for pure and catalyzed AP are summarized with reference to Rept. L0253-02-1 (not reviewed) for Aerojet data on AP to 1500 psig. Ref. 112 is cited for rate data on ANP-2744AF and ANP-2639AF propellants.

- 003 See Ref. 114.

- 004 O. R. Irwin, P. K. Salzman, W. H. Andersen, Aerojet-General Corp., Summary Rept. No. 0253-05 (21) FP, 54 pp. (June 26, 1963) (Confidential).

Pure AP and AP Propellants. Cites pure AP and AP propellants data of Refs. 101 and 114 with data of Ref. 009 as comparison for pure AP.

Fuse-wire and pressure-rate-of-rise burning rate data for pure AP agreed within an average error of 17% (above 5000 psi), purportedly verifying that "flashing" did not cause observed transition and hence transition is a real effect.

004 Continued

The possibility of a change in kinetic mechanism due to more exothermic surface reaction at high pressure is commented on, but this view is discounted by claims that the normal surface regression law (presumably Shultz and Dekker's Arrhenius-type rate law from "Transition-State Theory of the Linear Rate of Decomposition of Ammonium Perchlorate," Sixth Symposium (International) on Combustion, Reinhold, New York (1957), 618-626.) is sufficient to explain detonation of pure AP via a grain-burning model. It is conceded however, that "little direct information is available at present to evaluate the possibility of change in mechanism of the gas phase kinetics at high pressures." Also mentioned is the similarity between AP and AP-propellant burning-rate pressure dependence and the abrupt burning rate transitions observed by Taylor ("The Burning of Secondary Explosive Powders by a Convective Mechanism," Trans Far. Soc., 58, 561-568 (1962)) with porous RDX, PETN, HMX and by Whittaker ("Burning Rate Studies-Pt. 2: Measurement of the Consumption Rate of Nitroparaffin Fuels with Nitric Acid and the Effect of Varying the Viscosity of these Systems," U. S. Naval Ordnance Test Station NAVORD Report 1999, Pt. 2, (March 31, 1955)) with liquid bipropellants undergoing turbulence and liquid breakup at high burning rates (high pressures). It is suggested that crystal-habit changes may also contribute to transition (e.g. silver azide fracture during burning).

An expression for an increase in apparent burning rate (mass flux based on nominal area) due to temperature-gradient- and pressure-induced shear fracture at burning surface (with attendant burning-area increase) is derived. The derivation is based on an Eyring creep-rate fracture model and the resultant burning rate law after transition is $r = a \sinh (bP)$ for $P \geq P_{\text{transition}}$. (See also: O. R. Irwin, P. K. Salzman, W. H. Andersen, "Mechanism of the Accelerated Burning of Ammonium Perchlorate at High Pressures"; AIAA Journal, 1, 1178-1180 (1963).)

Pure AN. Burning rate data above 9000 psi (low-pressure deflagration limit) for $\frac{5}{8}$ "-diam. \times $1\frac{1}{2}$ " strands of pressed (ram pressure: 80,000 psi), unground AN (1.724 gm/cm^3 , 99% theoretical for β -phase AN) coated with Goodyear Pliobond and wrapped with Pliobond-coated asbestos paper. Considerable scatter in the data precluded definition of a well-defined rate law and was attributed to strand flaws and possible AN phase transitions.

004 Continued

TNT. Previous Aerojet Crawford-bomb rate data for $4 \times 4 \times 38$ mm strands was scattered and did not agree with the TNT data of Wachtell ("Anomalous Ballistic Behavior of Propellants under Extreme Pressure Conditions," Picatinny Arsenal, Tech. Memo. 1228, 14 pp. (July 1963)). The data of this report for $\frac{5}{8}$ " diam. $\times 1\frac{1}{2}$ " pressed (80,000-psi ram pressure) strands with Acryloid resin inhibition and nichrome wire ignition between 1000 and 30,000 psig showed much less scatter and were 10 to 25% lower than Wachtell's (with slightly lower slope) but did not exhibit Wachtell's reported transition at 5000 to 6000 psi.

005 See Ref. 118

006 R. Friedman, R. G. Nugent, K. E. Rumbel, A. C. Scurlock, "Deflagration of Ammonium Perchlorate," AFOSR (Atlantic Research Corp.) TN-56-206; 12 pp. (May 1956).

Crawford burner rates for pressed AP strands from 300 to 5000 psia. Not reviewed; superseded by later publications (e.g., Ref. 008).

007 R. Friedman, R. G. Nugent, K. E. Rumbel, A. C. Scurlock, "Deflagration of Ammonium Perchlorate," Sixth Symposium (International) on Combustion, Reinhold, New York (1956), 612-618.

Crawford-burner, unrestricted-strand burning rates in N_2 for pure pressed (1.894 to 1.908 gm/cm³) AP and AP pressed with 3% CC, CuO, Cr₂O₃, Fe₂O₃, MnO₂, or NaMnO₄ · 3H₂O between 40 and 350 atm. Pure AP data for various original particle sizes typically showed a rapidly decreasing rate with increasing pressure above 150 to 200 atm. Later work (009) attributes decreasing rates to convective cooling at strand edges. Temperature of product gases measured with 25-micron thermocouples (Pt|Pt-10% Rh) in transverse drilled holes were 900 to 1000°C (calculated: 1140 to 1180°C between 0 and 200 atm.), including scatter and pressure variations between 50 and 140 atm. Product gases for AP with CC appeared to be about 25 C° higher. Thermocouple size was varied and a ceramic bead coating was used to check possible catalytic effects; results were negative in each case. Calculated product equilibrium composition at 100 atm is given.

- 008 R. Friedman, J. B. Levy, K. E. Rumbel, "The Mechanism of Deflagration of Pure Ammonium Perchlorate," AFOSR (Atlantic Research Corp.) No. TN-59-173, 29 pp. (February 5, 1959).

Ref. 009 is based on this report and those subjects discussed in that reference are covered completely. Additional work included in this report but not in Ref. 009: infra-red photographic study of the burning surface and its temperature and an appendix describing analysis of a mathematical model for a burning homogeneous solid propellant including an external radiant flux. Lack of knowledge of the burning-surface emissivity precluded accurate surface temperature measurement, but an upper limit of 816°C was calculated assuming an estimated minimum burning-surface spectral emissivity of 0.2 at 500 psi.

- 009 J. B. Levy, and R. Friedman, "Further Studies of Pure Ammonium Perchlorate Deflagration," Eighth Symposium (International) on Combustion, Williams and Wilkins, Baltimore (1962), 663-672.

Crawford-burner rates for pure, pressed AP strands (4 × 4 × 38 mm) in nitrogen from 330 to 5000 psia.

More energetic ignition extended the lower pressure deflagration limit of pure, pressed AP strands to 330 psia., and asbestos-wrapping restriction eliminated the previously-reported (007) upper pressure deflagration limit.

Studies of pressed pure and CC-catalyzed AP strands burning with externally-applied radiative flux (to 18 cal/cm²-sec) in 1 atm. of nitrogen are reported. Some work is mentioned involving CaO, MgO, and MgClO₄ in place of CC. Below 10 cal/cm²-sec pure AP did not burn but sublimed very slowly. Above the minimum flux levels required to support burning, each formulation showed burning rates increasing linearly with flux. Zero-flux intercepts of r vs. applied flux plots are suggested as measures of chemical rate enhancement by the catalyst, while increasing slopes with increasing catalyst level are suggested to include this plus radiant energy absorptivity effects. Measured sample reflectivities at low temperature correlated inversely with increasing zero-flux intercept values and slopes on r vs. applied flux plots. A heat-loss-based deflagration-limit hypothesis is supported by inability to ignite samples at low ambient temperature (-18°C). The effects of CC concentration on both the lower and upper pressure limits of combustion are reported and discussed.

009 Continued

Product gas sampling for pure and catalyzed AP samples was carried out for pressures between atmospheric and 2000 psi. Major observations were that (1) NO content is pressure-dependent, dropping by a factor of two between atmospheric pressure and 1000 psi above which it levels off and (2) N₂O content is nearly constant up to 1000 psi and then decreases. Catalytic effects appeared confined to marked reduction of the observed concentration of N₂O. Strand cross sectional area affected N₂O yield strongly, and this is attributed to edge quenching effects.

Mechanistic explanations of product-gas trends involve NO formation from NH₃ and subsequent reaction with NH₃ to N₂O. It is suggested that a higher activation energy for the second reaction would explain the observed pressure dependency of NO in the product gas.

- 010 G. K. Adams, B. H. Newman, A. B. Robins, "Combustion of Propellants Based Upon Ammonium Perchlorate," Eighth Symposium (International) on Combustion, Williams and Wilkins, Baltimore (1962), 693-705.

A survey of work at E.R.D.E. (U.K.) carried out from 1951 to 1957, including studies of the effects of particle size, pressure, fuel-oxidizer ratio, and fuel composition on burning rate. Data are given for burning rates at up to 3000 psig. for pressed (6000 psi) $\frac{1}{2} \times \frac{1}{2} \times 8$ cm. strands of pure AP and AP with varying amounts of polystyrene, paraformaldehyde, carbon black, cellulose acetate, sucrose octaacetate, and mixtures of paraformaldehyde and carbon black. Some work is reported from 2-inch-motor firings of AP (particle-size-varied) in a cellulose acetate-triacetin-wetting-agent binder both with and without ammonium picrate (up to 60%) and of AP-polyisobutylene.

Pure AP strands were found to burn above about 1000 psi and rates were found sensitive to trace impurities. It was suggested that the low-pressure deflagration limit was observed not only because of radiative heat loss (see also Ref. 009) but also because of the pressure-dependence of the heat of decomposition (high NO content in product gas at lower pressures). Particle-size effects were slight among samples pressed from B.S.S. 240-300 mesh (58 microns), 200-240 mesh (70 microns), and 150-200 mesh (90 microns). Reported is $r_{1000} = 0.25$ to 0.27 in/sec, with n approximately constant between 1000 and 3000 psig at 0.5.

- 011 A. R. Glazkova, "The Effect of Pressure on the Rate of Combustion of Ammonium Perchlorate," Zh. Prikl. Mekhan. i Tekhn. Fiz. 1963, 121-125 (in Russian)

Burning rates for 5- to 15-mm-diam. pressed strands of pure ammonium perchlorate with various confinements and restrictor coatings and for pressures from 300 to 1000 atm. r-P plots typically display negative slopes near 200 atm, followed by high pressure indexes at higher pressures. A wide variation in rate at a given pressure is observed to depend on the nature of confinement and/or restrictor used (Plexiglas tubes, PVC coatings, fluorinated-grease coatings, no restrictor). Except for unrestricted samples, little effect of strand diameter on burning rate is observed.

Series 100-Inert-Binder Composite Propellants

- 101 D. V. Paulson, G. L. Roark, R. B. Christensen, A. Gaylord, R. D. Erickson, "Study of Solid-Composite Propellant Explosive Behavior in 3KS-1000-Size Motors (U)," Aerojet-General Corp., Quarterly Rept. No. 0253-01-307-4, 34 pp. (July 15, 1960) (Confidential)

Crawford burner, $\frac{1}{4}$ "-diameter-strand burning rates for ANP-Z propellant (75% KP, 24.5% PU, 0.5% CC) in 68-72°F. N_2 at five pressures between 400 and 10,000 psi. No $n > 1$ was observed.

Refers to Aerojet-General, No. 0253-01-307-2, for burning rate data on ANP-2639AF (see Ref. 111), ANP-2655AF (see Ref. 111) ANP-X (75% AP, 24.5% PU, 0.5% CC), ANP-Y (60% AP, 15% KP, 24.5% PU, 0.5% CC), and ANP-2652 EU Mod. 2 (70% AP, 12% KP, 17.5% PU, 0.5% CC).

A summary of this study appears in Aerojet-General Final Report No. 0253-01-307-6 (February 15, 1961).

- 102 M. Summerfield (Princeton Univ.), private communication on work done in conjunction with Picatinny Arsenal, December 1962.

Strand burning rates for PS-KP (75% bimodal) between 1000 and 20,000 psi showed a slightly decreasing pressure index with increasing pressure; $r_{1000} = 0.9$ in/sec., $n_{1000} = 20,000 = 0.62$. These data agree well with ANP-Z rates reported in Ref. 101.

- 103 M. Barrere, A. Jaumotte, B. F. DeVeubeke, J. Vanderkerchove, Rocket Propulsion, Elsevier, New York (1960), 196.

Burning rate curves between 700 and 4200 psi for Galcit formulation (AO-76.5% KP) at 60°, 15° and -30°C. Source of the data is not disclosed.

- 104 A. F. Belyaev, A. I. Korotkov, A. K. Parfenov, A. A. Sulimov, "Burning Velocity of Some Explosives and Explosive Mixtures Under Very High Pressures"; Zh. Fiz. Khim., 37, 150-156 (1963) (in Russian).

5-mm-diam. \times 2.5 to 3 mm. pressed cylinders of various explosive substances (TNT, PETN, black powder, 62% KP + TNT, 87% KP + asphalt, 79% AN + TNT) burned in closed bomb with alternation of layers disrupting recorded P-t signal for r-P determination at pressures from 200 to 4000 atm. Rates were checked using ionization probes, and agreement

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was good. The possibility of attributing the observed levelling - off of the mixed phase systems to mass diffusion effects is discussed inconclusively and the relation of the various data to detonation phenomena is considered.

105 _____, "Research and Development, U. S. Naval Powder Factory, " Third Quarterly Report for Fiscal 1958, 79-80 (March 14, 1958) (Confidential)

Qualitative results from closed bomb firings of Aerojet ANP-2592 EU (70% AP, 12% KP, 18% PU) at -60°F, 160°F as 1.25" diam. rods and single-perforation cylinders. Maximum pressure attained: 75 kpsi. Only 60°F results showed abrupt dP/dt increase, presumably due to grain break-up; previous work with 0.7"-diam. samples reportedly showed some evidence of irregular (grain break-up) burning. No quantitative data given.

106 _____, Quarterly Progress Report on Propellant Chemistry, Rohm & Haas Company, Rept. No. P-54-10, 6-8 (August 25, 1954) (Confidential).

Burning rate data between 1000 and 20,000 psi for strands ($\frac{1}{8}$ "-sq. $\times \frac{1}{2}$ "-long) of polyvinyl ethyl ether with (0 to 85%) AP and (80 to 0%) potassium dinitroacetonitrile and of high molecular weight polyisobutylene-85% AP. Both propellants reportedly displayed $r_{1000, 25^\circ\text{C}} = 1.0$ in/sec and $n = 0.6$ over the whole pressure range but neither data nor plots are shown.

Strands were prepared by dissolving binder polymer in solvent (petroleum ether on n-hexane), mixing with oxidizer, drying under vacuum (30 mm Hg) at 90°C for two hours, and pressing into die of desired form at 90°C.

107 _____, Quarterly Progress Report on Propellant Chemistry, Rohm & Haas Company, Rept. No. P-55-2, 2-3 (February 25, 1955) (Confidential)

Crawford bomb burning rates for $\frac{1}{8}$ "-sq. $\times \frac{1}{2}$ "-long strands of RDX-2% polyvinyl ethyl ether prepared by solvent-drying (followed by pressing at 50,000 to 75,000 psi) and burned between 6000 and 20,000 psi in nitrogen at -40°, 25° and 60°C. The organic binder, a pressure-sensitive adhesive, was used following failure in attempts to produce well-consolidated, pressed strands of pure RDX. Within experimental scatter, no difference was observed in r-P plots for initial temperatures of 25° and 60°C but an abrupt change in pressure

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index ($n = 0.84$ to $n = 1.04$) was observed at about 5300 psi. The r-P plot for -40°C coincided with the 25° and 60°C plots at high pressure with $n = 1.04$ but displayed this high index to pressures as low as about 3000 psi below which a lower index (0.90) is reported.

Burning rates for $\frac{1}{8}''\text{-sq} \times \frac{1}{2}''\text{-long}$, solvent-dried, pressed strands of polyvinyl ethyl ether-85% (6 μ) KP between 1000 and 20,000 psi at four pressures (25°C) and at three pressures (-40° , 60°C) showed a trend to decreasing pressure index with increasing pressure and also low temperature coefficients (0.11%/°C at 10,500 psi).

r-P data for solvent-dried, pressed strands of polyvinyl ethyl ether-85% (10 μ) AP between 1000 and 20,000 psi showed a pressure index decrease to $n = 0.55$ at 20,000 psi (r_{20000} , $25^{\circ}\text{C} = 5$ in/sec) from $n = 0.64$ at 1000 psi. No abrupt transition was observed but data are from only four pressures in the range. r_{1000} ($= 0.80$ in/sec) is reported 20% higher than in Ref. 106 for the same propellant.

- 108 D. C. Vest, R. W. Green, R. A. Sault, B. B. Grollman, "A Qualitative Discussion of the Burning Mechanism of Porous Propellants," Bull. 10th Mtg. JANAF Solid Prop. Group, II, 333-356 (June 1954) (Confidential)

Closed bomb r-P data from BRL are given for M-7 - (55% to 75%) AP, PS-67% AP, cord nitrocellulose, and nitrocellulose-50% and 60% NaCl (leached) in the range 2000 to 30,000 psi. High indexes ($n = 1.28$ to 2.3) were observed for the AP and leached NaCl nitrocellulose propellants. Some samples were pressed after casting. Liquid dye penetration of samples at hydrostatic pressures of 1000 to 10,000 psi was observed. No details concerning experimental technique are reported but may be contained in BRL Report 902 (April 1954 with the same authors and title as this paper).

A "porous-burning" mechanism is postulated for heterogeneous propellants and is discussed in the light of closed bomb r-P data.

- 109 K. P. Hall, J. Wenograd, R. B. Cole, "Burning Rate Control Factors in Solid Propellants, " Princeton Univ. Dept. of Aero. Eng., 11th and 12th Quarterly Technical Summary Report Nos. 446 K and L, 16 pp. (March 21, 1962).

Strand burning rates from 30 to 20,000 psi for two bimodal oxidizer (70%, 200 μ , 30%, 20 μ) propellants, one, PBAA-AP (75%), the other, PS-AP (75%); also for two PS propellants (65 and 70% AP) with two oxidizer particle sizes each (9 μ , 140 μ ; 20 μ , 200 μ , respectively).

Small particle sizes with PS fuel gave rate increases as much as 50 to 75% and exhibited a greater tendency toward a plateau between 1000 and 4000 psi than bimodal oxidizer sizes. Unimodal oxidizer propellant curves converged above about 4000 psi, with pressure indexes exceeding unity. The PBAA-fuelled, bimodal-oxidizer propellant exhibited up to 50% lower rates and a greater tendency toward a plateau (1000-4000 psi) than the corresponding PS propellant but the bimodal oxidizer propellant rates converged above 4000 psi with a pressure index near unity above 10,000 psi.

- 110 _____, "Advancement of Solid Propellant Rocketry, " Thiokol Chemical Corp. (Huntsville Division), Quarterly Progress Report No. 35-61, 182 pp. (August 3, 1961) (Confidential).

Burning rate data for TP-H8041 propellant (PBAA/ERL1 16%; AP 68%; Al (atomized powder) 16%) from strands (600 to 3900 psi) and (erosively) from grains in blast tube (300 to 4000 psi).

- 111 J. L. Chaille, Rohm & Haas Company, unpublished data, January 1965.

- 112 _____, "Polaris Deflagration to Detonation Transition Studies, " Aerojet-General Corp., No. GWR 3567-02-445, Progress Report No. 5, (August 15, 1959) (Confidential)

Original data (cited by Ref. 111) on ANP-2639 AF and ANP-2744 AF propellant burning rates between 1500 and 14,000 psi. (Not reviewed)

- 113 _____, "Polaris Power Plant Development"; Aerojet-General Corp., No. 3520-01M-28, 77 pp. (February 20, 1960) (Confidential)

Crawford burner strand burning rates for ANP-2639AF (see Ref. 114) from 10,000 to 23,000 psi indicated decrease of pressure index to 0.91 at 12,500 psi following transition to $n = 1.87$ at 5000 psi.

Underwater burning of restricted and unrestricted strands showed that lack of restrictor was not a problem even at high pressures in water.

- 114 O. R. Irwin, W. H. Andersen, R. D. Erickson, "Susceptibility of Solid-Composite Propellants to Explosion or Detonation," Aerojet-General Corp., Final Summary Report 0253-02-12, 50 pp. (April 20, 1961) (Confidential)

Crawford bomb strand burning rate data between 1500 and 14,000 psi for ANP-2744 AF (70% AP, 8% Al, 22% PU) and ANP-2639 AF (60% AP, 15% Al, 25% PU) reported from Ref. 112, showing transition to $n = 2$ at 5000 to 6000 psi.¹ Similar transition is reported for ANP-2592 EU (70% AP, 12% KP, 18% PU), "X" propellant (75% AP, 24% PU) (ANP-2639 AF without aluminum), and ANP-2655 AF (70% AP, 8% Al, 22% PU) with data between 3700 and 12,000 psi before and after kneading.

Similar data for $\frac{5}{8}$ "-diam., Pliobond-coated and asbestos-paper-wrapped, pressed AP strands burning between 1000 and 23,000 psi. Abrupt transition was observed with a pressure index exceeding unity above 5000 psi. Rates were checked by records from "burn-by" thermocouples in strands.

Unrestricted 4 mm square strands gave results similar to those of Ref. 007. Difficulty with both "flashing" and depressed rates with various restriction techniques is mentioned.

The plot of r - P data obtained for pure AP exhibits approximately $\pm 10\%$ scatter about the fitted straight line segments used to approximate it.

- 115 O. R. Irwin, W. H. Andersen, P. K. Salzman, "Susceptibility of Solid-Composite Propellants to Explosion or Detonation," Aerojet-General Corp., Final Summary Rept. 0253-02 (16) FP, 40 pp. (April 3, 1962) (Confidential).

¹ Various plots of these data indicate different slopes at pressures below transition but all indicate abrupt transition between 4500 and 5000 psi. These data are at variance with those of Ref. 101.

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Closed bomb burning rates for $\frac{1}{2}$ "-diameter ANP-2639 AF (see Ref. 111) strands from 5000 to 15,000 psi. show transition to $n = 2$ above 5000 psi ($r_{5000} = 0.34$ in/sec) with no effect of rate of pressure change (produced by variable venting during burning¹; dP/dt between ± 2500 psi/sec). In one run, change in pressurization rate resulted from burning last part of a strand two-thirds submerged in water while the first one-third burned above water. Pressurization rate consequently changed in closed bomb from high rate to almost zero (presumably due to product gas quenching by water). Both rates fell on $n = 2$ portion of r - P curve. Explanation proposed: once high pressurization rate initiates "porous burning", removal of applied stress does not allow immediate reversion to normal burning, implying that pressure or dP/dt inside pores is important feature.

Eight burning rate data points at two pressures (10,000 and 20,000 psi) for $\frac{1}{8}$ " diameter strands (lower pressurization rates) were indistinguishable from larger strand data considering scatter of other data (discrepancy in normal strand diameters quoted: $\frac{1}{4}$ " vs $\frac{1}{2}$ ").

Closed bomb burning rates for pressed (80,000-psi ram pressure) AP-KP (80%-20%) and AP-KCl (89%-11%) $\frac{5}{8}$ "-diameter restricted strands (restricted as previous pure AP strands, described in Ref. 114, with Plibond-coated asbestos paper) using fuse wires over 2 half-inch increments of length starting $\frac{1}{4}$ " from ignition end. Pressures of 1250, 2800, 10,000, and 20,000 psig with 4 rate measurements at each (2 strands at each). Extreme scatter purported to characterize each composition in this and later reports (e.g., Ref. 004)

r - P plots for KP and KP-AP propellants (ANP-Z and ANP-Y, respectively) between 1000 and 8,000 to 20,000 psi are reproduced from Ref. 101. The absence of a strong transition effect in KP propellant is reported to be insufficiently explained by liquid-phase effects and a higher fracture energy and/or a drastically changed decomposition mechanism is suggested instead.

- 116 D. D. Perry, "High Energy Solid Propellant Investigations (Final Report, April 12, 1954, to June 3, 1956), " Reaction Motors, Inc., Final Rept. No. RMI-035-F, 129-135 (June 1, 1956) (Confidential)

$\frac{1}{8}$ "-diam. \times 4"-long strand burning rates (at 70°F) between 200 and 3000 to 4000 psig (in N_2) for four acetylenic polyurethane propellants (polyformal: 23.1, 25.8, 25.9%; 4, 4'-diisocyanato-diphenylurethane: 4.5, 5.1, 6.15%; AP: 72.4, 69.1, 68%; and

¹ Scatter of data raises doubt regarding reported linearity of curve and may actually suggest better fit to a curved plot.

polyformal: 23.4%; 2,4-toluene diisocyanate: 4.0%; AP:72.6%) were found linear with $r_{1000} = 1.15, 0.75, 0.62, 0.79$ in/sec, respectively, and $n_{1000} = 0.40, 0.27, 0.28, 0.28$, respectively.

- 117 G. W. Batchelder, and C. A. Zimmerman, "New Burning Rate Accelerators for Aeroplex Propellants"; Bull. 9th Mtg. JANAF Solid Prop. Group, I, 235-240 (1953).

Burning rate curves from "Midget" motor firings at Aerojet-General between 450 and 4500 psia. and at -50° , 60° and 150° F for AN-581W propellant of 85% AP, 3.6% polyester (VP-33A), 9.3% n-butyl acrylate, 1.4% methyl acrylate with 1% DC-992 (Dow-Corning) silicone resin (catalyst). All three temperatures gave linear r-P plots with $n = 0.61$ (r_{1000} , 60° F = 0.63 in/sec) with the modified (AN-581 Mod II) propellant while the unmodified propellant showed $n = 0.46$ (r_{1000} , 60° F = 0.40 in/sec.) up to 2000 psi.

Addition of other siliceous catalysts (including conventional petroleum-cracking catalysts) gave varying effects reported only in terms of r_{1000} , 60° F (up to 0.80 in/sec with Bentone 18 bentonite) and $n = 0.55$ (Bentone 18-DC-992 resin). Most additives raised r_{1000} appreciably or not at all (0.41 to 0.80) but depressed or increased n slightly (0.30 to 0.55). AN-581 Mod II exhibited a different flame appearance (burning in air) than the base AN-581W propellant without silicone additive: "A narrow, intensely luminous band of flame was observed close to the surface . . . the effect was quite similar to that of a Welsbach mantle, and it was speculated that silica formed during combustion was the catalytically-active agent."

- 118 M. L. Rice, K. E. Rumbel, L. L. Weil, A. W. Sloan, T. J. O'Donnell, A. C. Scurlock, "Research and Development Programs in Fields of Solid Propellants and Interior Ballistics," Atlantic Research Corp., Quarterly Progress Rept. No. 19, 14 pp., April 1955 (Confidential):

Propellant burning studies including photographic investigations of strands containing short wires, effects on burning rate and pressure index of several catalysts, Arcite propellant temperature coefficients, and burning of pure and modified AP.

Temperature coefficient studies include r-P data for strands (of unspecified size, but probably 4 mm sq. as in (007)) of Arcite 155X (25% Exon 654 [PVC] + plasticizer, 75% AP), Arcite 208X (24% Exon 654 + plasticizer, 75% AP, 1% CC), and Arcite 287/T2 (25% Exon 654 + plasticizer, 74% AP, 1% CB) from 15 to 5000 psi at -20 , 70 , 165° F. r-P plots

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are inverted S-shape with $n_{5000} = 0.53$ to 0.85 , $n_{1000} = 0.33$ to 0.42 and show a general trend to increasing index at high pressures. Plots for different initial temperatures are essentially parallel.

r-P data for pressed AP strands with and without 1.3% CC, Bentone 18 and 34, CaCO_3 and CaO between 400 and 5000 psi (different pressure ranges for different compositions) and for three pressing pressures (50,000; 75,000; 100,000 psi). Strand densities and burning rates for pure AP were found to be independent of pressing pressures. r-P relations including pressure limits were found sensitive to composition. While CC addition increased the low-pressure deflagration limit (in contrast to its action in Arcite propellants), it also substantially increased the burning rate and upper pressure limit of steady burning. The two Bentone additives were found to decrease AP burning rates (contrary to their action in propellant). It was concluded that the Bentones must be effective in catalyzing either the organic binder pyrolysis or the oxidizer-binder pyrolysis products reactions while CC probably catalyzes the AP decomposition. The fact that combined use of CC and the Bentones in AP propellants gives an additive burning rate enhancement is held to corroborate this view of two different catalytic mechanisms.

- 119 K. E. Rumbel, M. Cohen, C. B. Henderson, A. C. Scurlock, "A Physical Means of Attaining High Burning Rate in Solid Propellants," Bull. 11th Mtg. JANAF Solid Prop. Group, I, 155-175 (May 1955) (Confidential).

Data of Ref. 118 on strand burning rates for several Arcite (PVC-AP(75-80%)) propellants with embedded metal wires (20-5000 psi) and without wires (20-2000 psi). No apparent tendency toward high index at high pressures; S-shaped r-P curves with metal wires, nearly linear r-P curves (slightly concave downward) without wires. Wire materials were copper, silver, tungsten, molybdenum, steel, aluminum, magnesium.

- 120 G. L. Roark, D. V. Paulson, L. R. Codner, "Evaluation of Polaris A3 Leading Candidate Propellants for Their Explosive Behavior," Aerojet-General Corp., Quarterly Progress Rept. 0253-04(08) QP, 17 pp. (July 31, 1962) (Confidential).

ANP-3004LE (32% AP, 32% RDX, 18% Al, 18% PU) propellant burning rates from 1 atm. to 8000 psi. Not reviewed; this report appears to have been discussed comprehensively in Refs. 118 and 119.

- 121 L. R. Codner, "Evaluation of Polaris A3 Leading Candidate Propellants for Their Explosive Behavior," Aerojet-General Corp., Quarterly Progress Report 0253-04 (10) QP, 17 pp. (January 25, 1963) (Confidential).

Strand burning rate data for ANP-3004LE (see Ref. 121) between 1500 and 5000 psi, indicating an S-shaped r-P curve with $n < 1$ below about 3500 psi, > 1 above 3500 psi and below 4000, and ≈ 1 above 4000 psi. The small number of data points reported makes these trends questionable. 3-KD-900 motor firings with ANP-3004KD (slightly different oxidizer particle size) indicated transition in 2000- to 3000-psi range (nozzle insert ejection).

- 122 L. R. Codner, R. D. Erickson, D. V. Paulson, "Evaluation of Polaris A3 Leading Candidate Propellants for Their Explosive Behavior," Aerojet-General Corp., Final Rept. 0253-04(11) FP, 72 pp. (June 28, 1963) (Confidential).

Closed bomb strand burning rates for ANP-3004 LE (see Ref. 121) and ANP-3004-KD4 at several different pressures showing transitions from $n < 1$ to $n > 1$ at 3500 and 2500 psi, respectively. The only reported difference between these compositions is AP particle-size distributions (LE: 60%, + 48; unground; 20%, high-speed Mikropulverized; KD4: 72%, + 48; 23% unground; 5%, high-speed Mikropulverized).

- 123 _____, "Investigation of the Mechanism of Decomposition, Combustion and Detonation of Solids," Aerojet-General Corp. (Azusa), Rept. No. 0372-01-6, 13 pp. (June 30, 1961).

Hot plate pyrolysis data on strands of RDX pressed at 40,000 psi with 3% polystyrene (strand density = 1.614 gm/cc) between 215 and 410°C (1 atm). Photographically-determined burning rates for $\frac{5}{8} \times \frac{1}{4}$ -in. cylindrical strands of RDX-polystyrene at four pressures (5 strands) between 13.6 and 95 atm. These data were fitted by $n = 0.46$ within the scatter observed on the two duplicate firings. Other work described deals with the bulk decomposition of NH_4F between 22° and 115°C, an apparatus for study of the ammonia-perchloric acid gas-phase reaction, and decomposition of perchloric acid.

- 124 _____, Quarterly Progress Report on Propellant Chemistry,
Rohm & Haas Company, Report No. 54-16, 16 (November 25, 1954)
(Confidential)

Photographically-determined burning rates for pure, pressed RDX with $r_{1000} = 0.45$ in/sec and $n = 0.75$ (500 to 2000 psi) are specified. No sample size, details of technique, or data are reported.

- 125 _____, Quarterly Progress Report on Propellant Chemistry,
Rohm & Haas Company, Report No. P-55-8, 10 (May 25, 1955)
(Confidential)

Strand burning rate data for polyvinyl ethyl ether and 85% RDX reported as r_{1000} , $25^\circ \text{C} = 0.1$ in/sec, $n = 0.7$ (1000 to 3000 psi). No experimental details or data are reported.

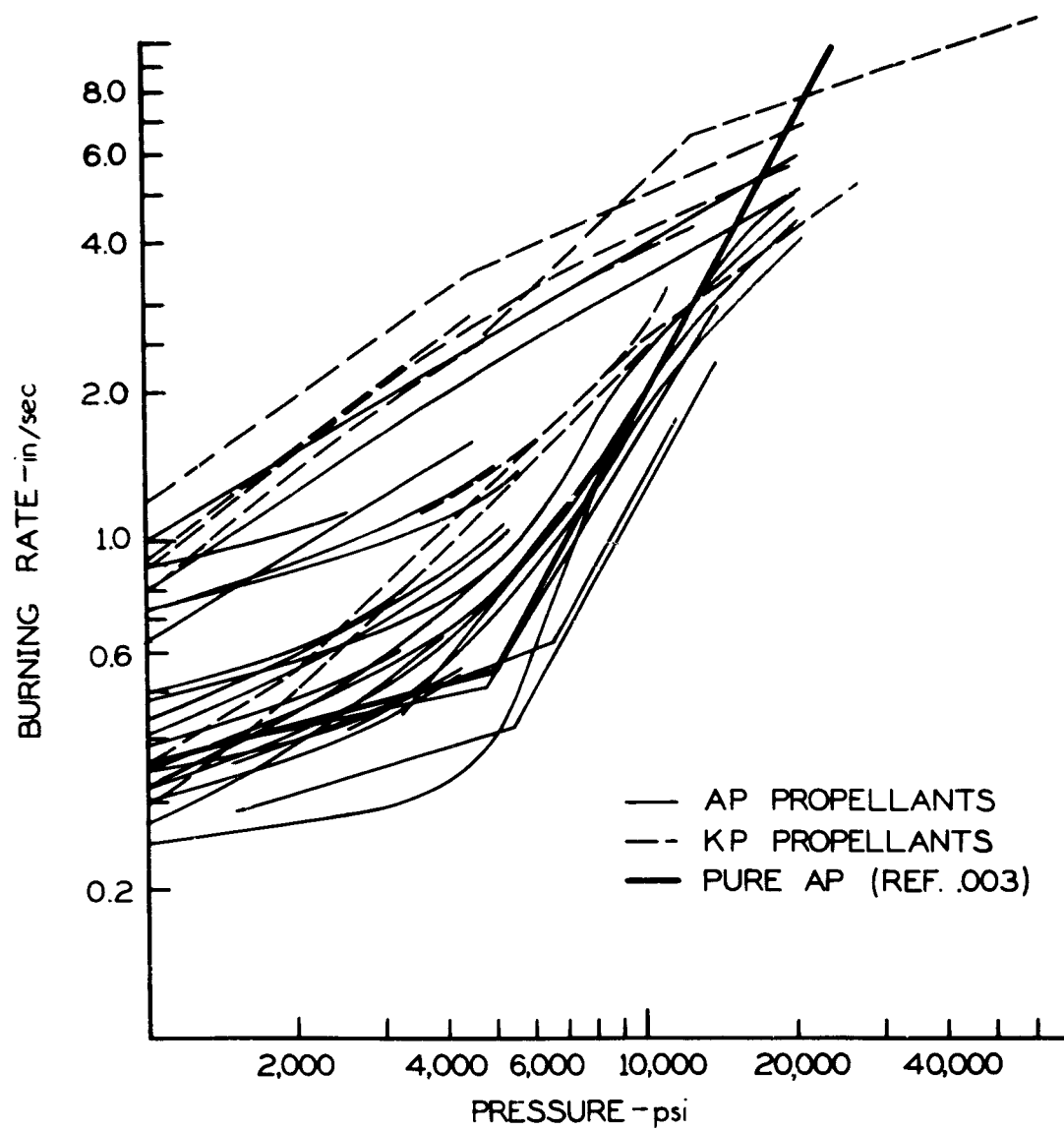


Fig. 1 Collected high pressure r-P data for inert-binder propellants.

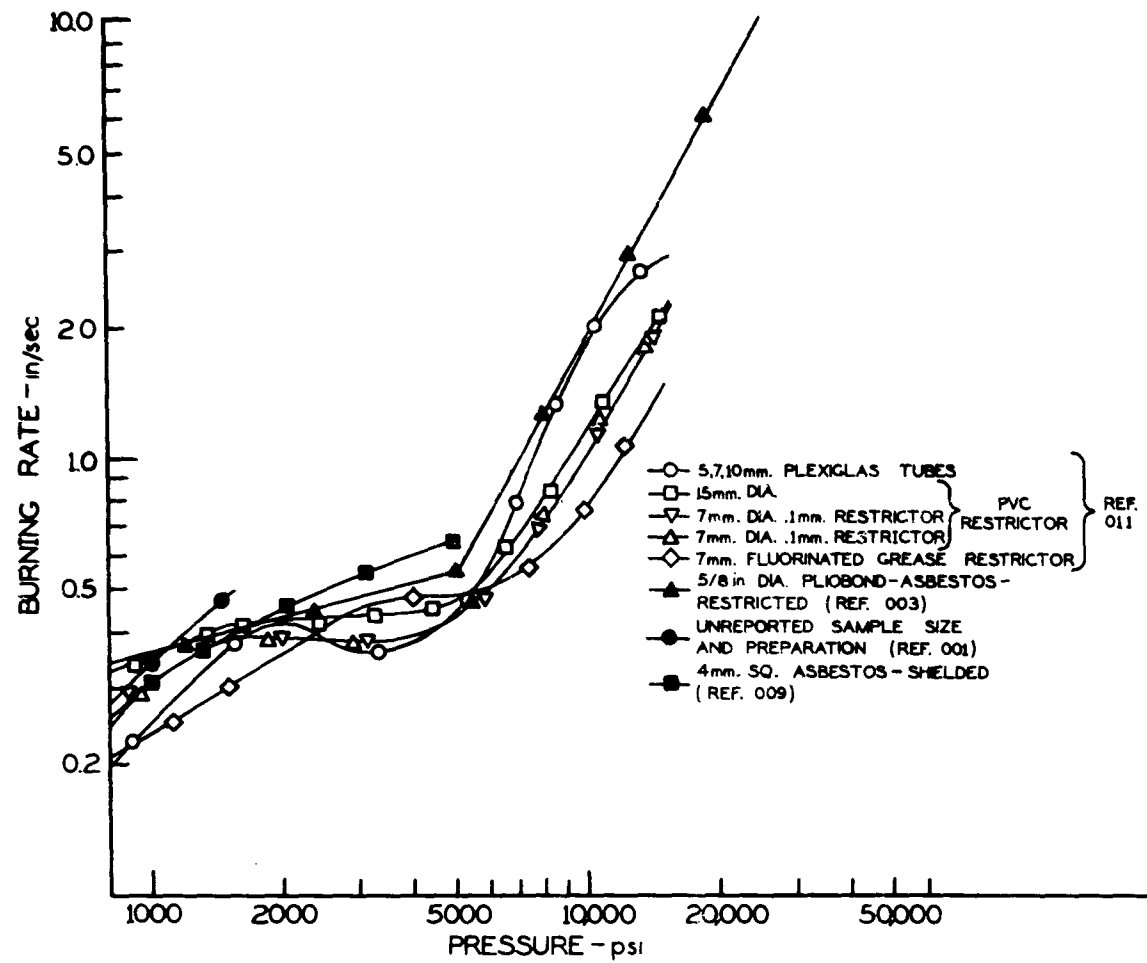


Fig. 2 High pressure r-P data for restricted, pressed NH_4ClO_4 strands.

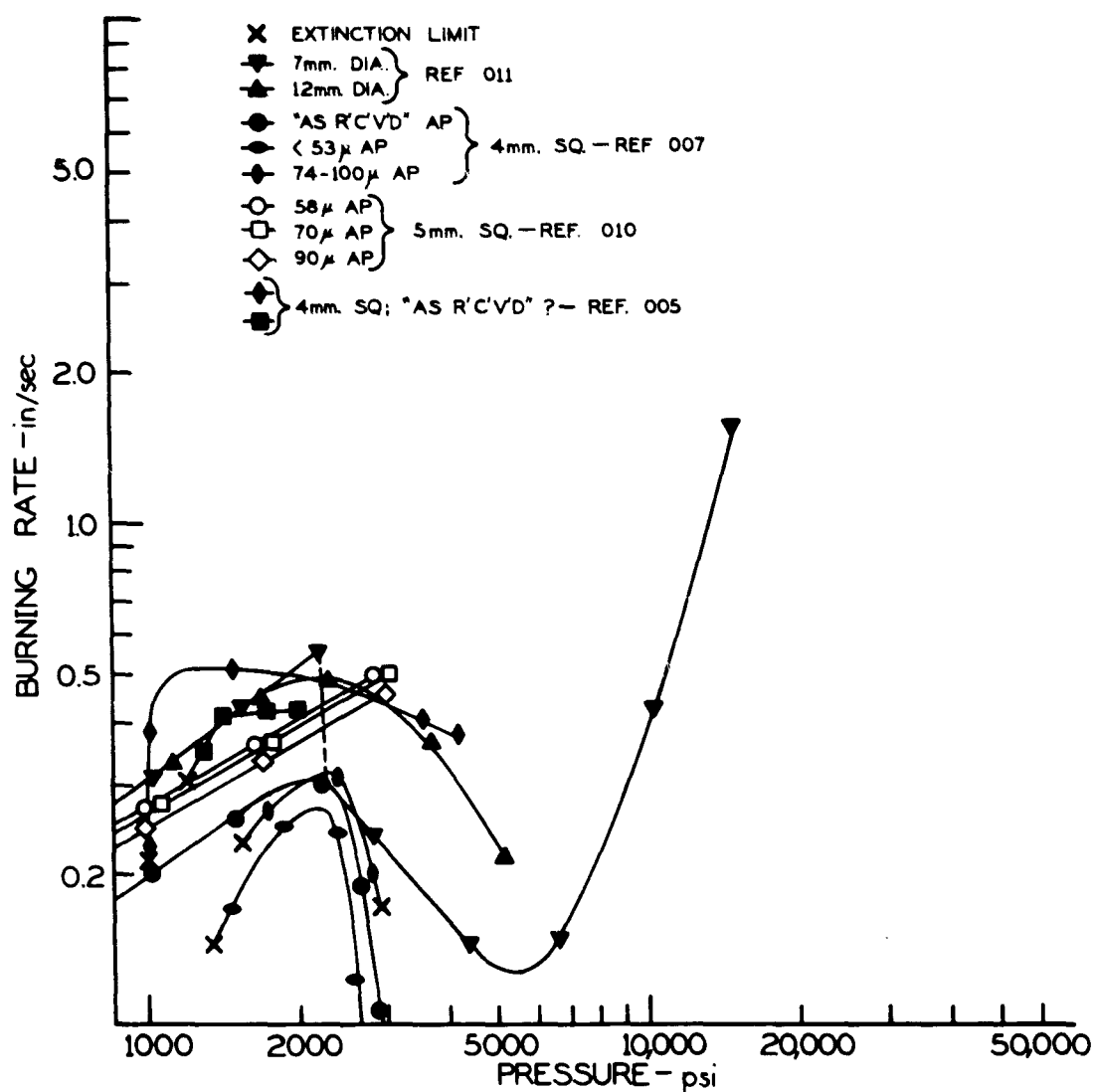


Fig. 3 High pressure r-P data for unrestricted, pressed NH_4ClO_4 strands.

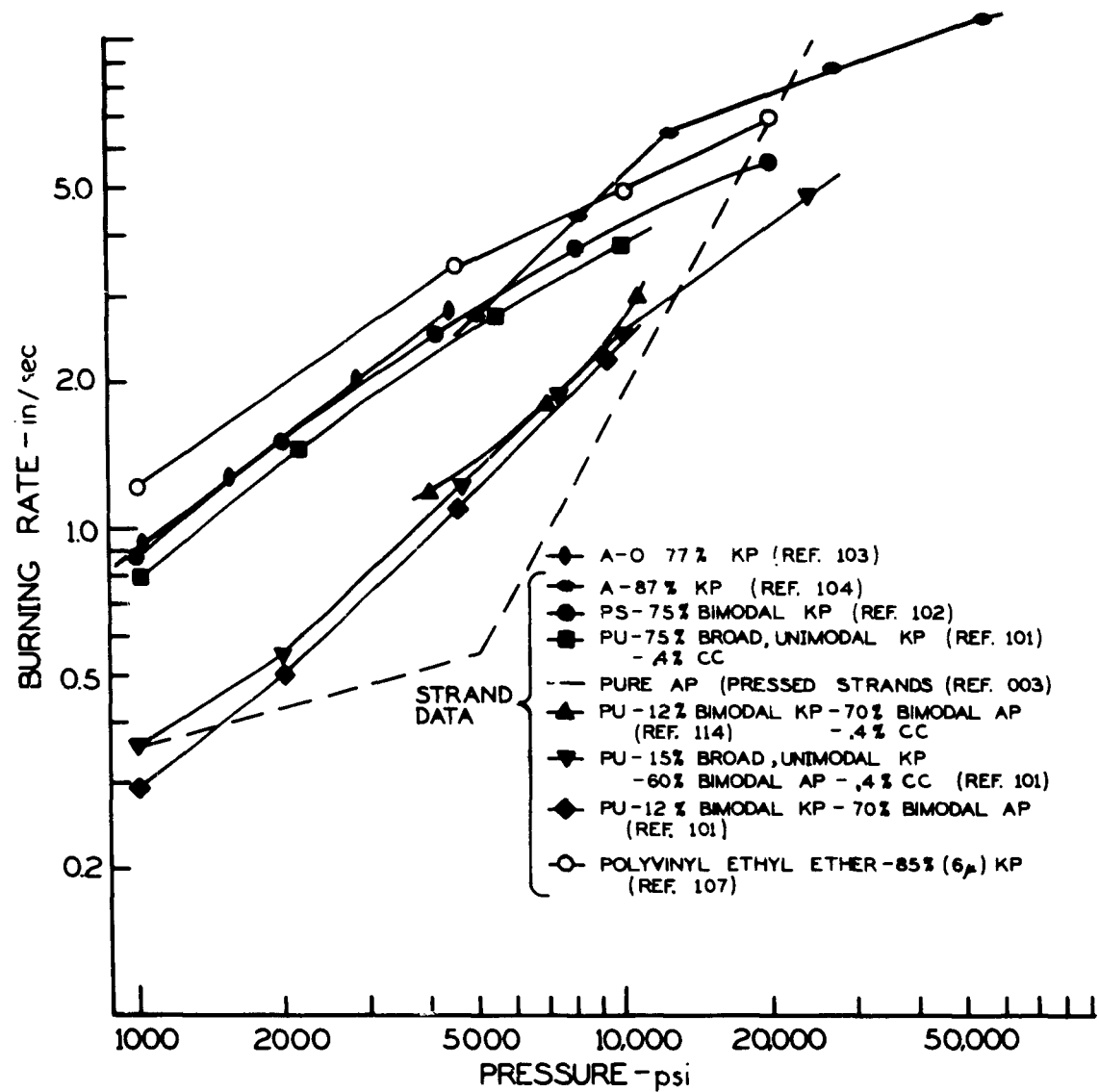


Fig. 4 High pressure r-P data for inert-binder propellants with KClO_4 oxidizer.

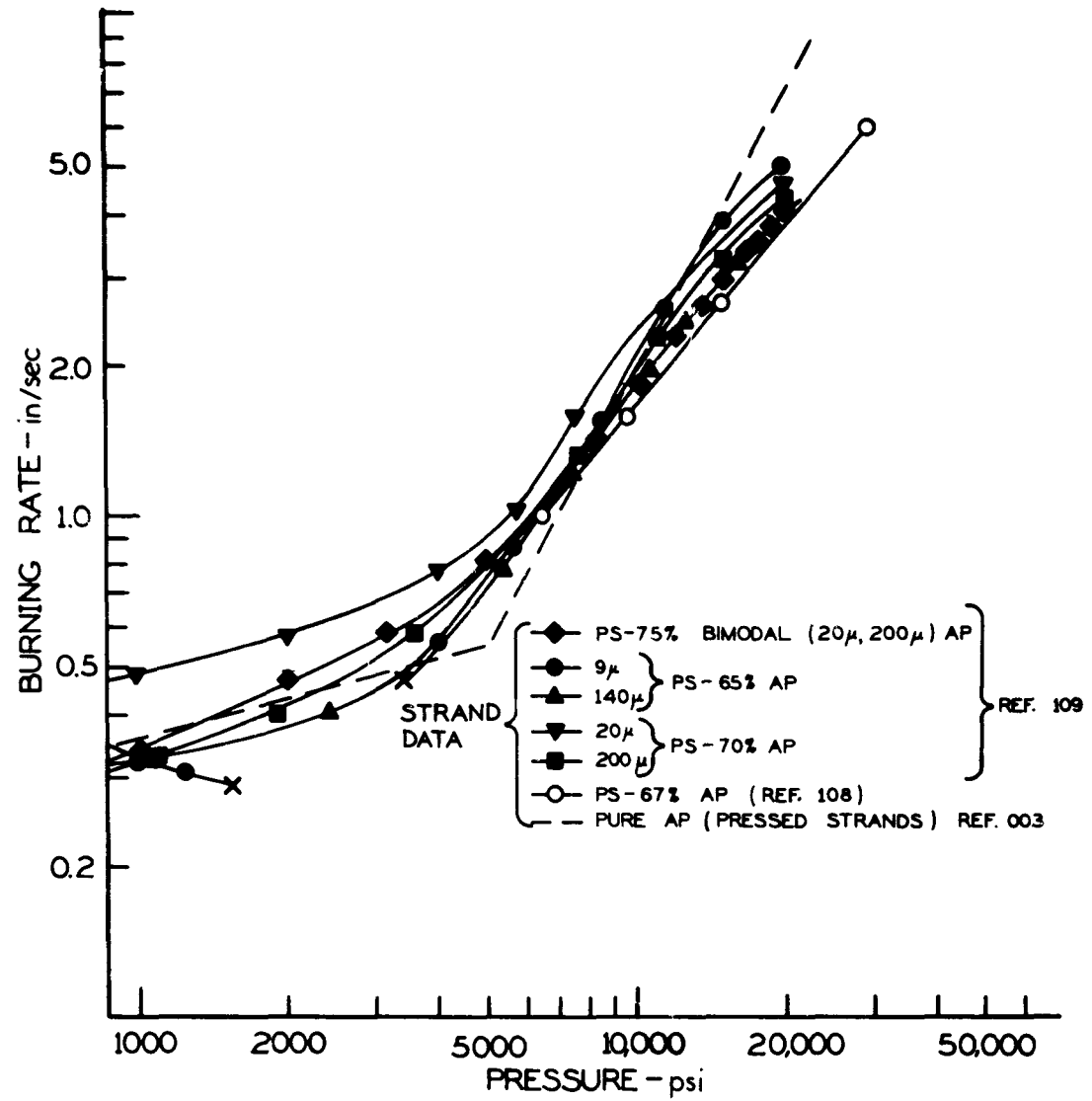


Fig. 5 High pressure r-P data for polysulfide-NH₄ClO₄ propellants.

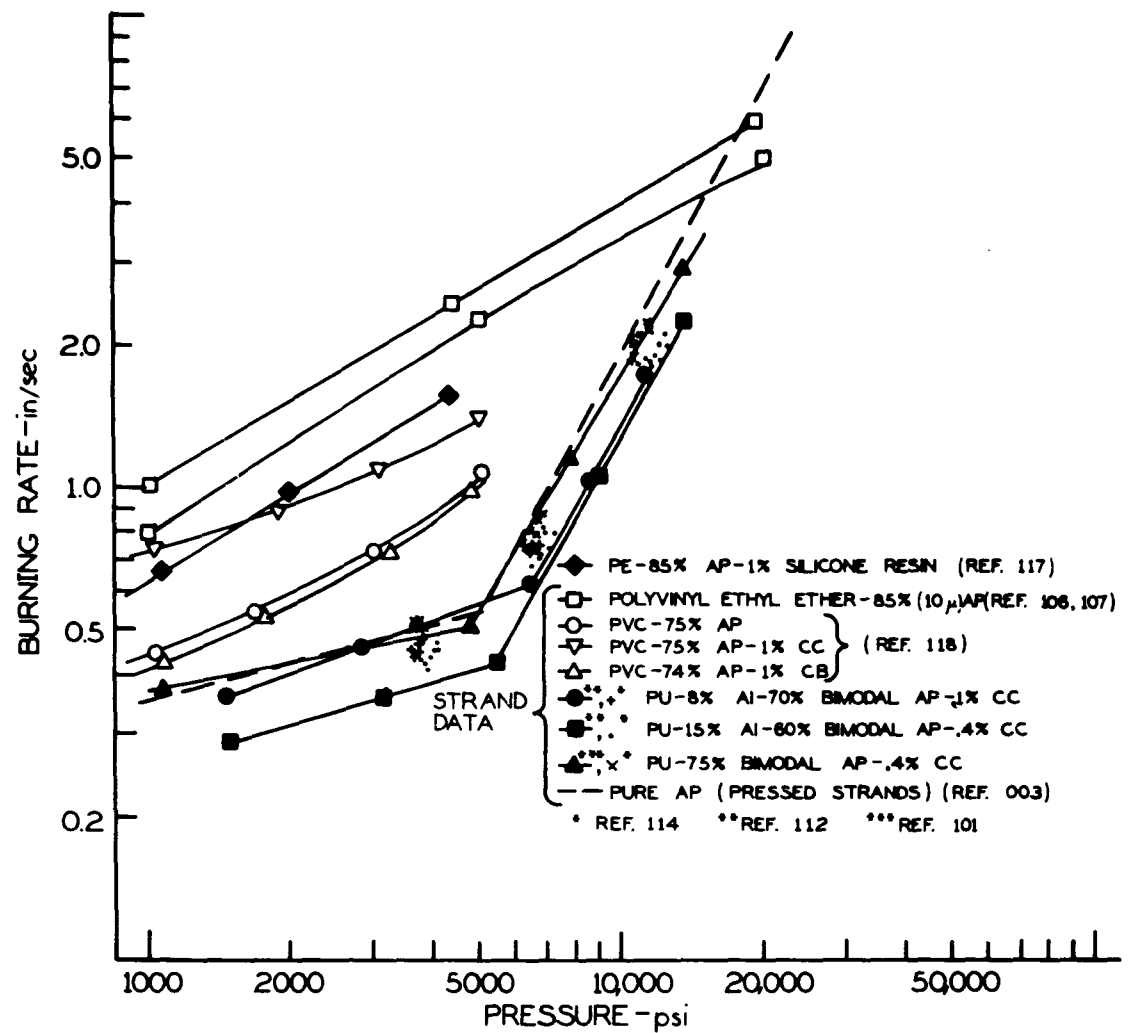


Fig. 6 High pressure r-P data for NH_4ClO_4 -oxidized polyurethane, polyvinyl chloride, and polyester-acrylic propellants.

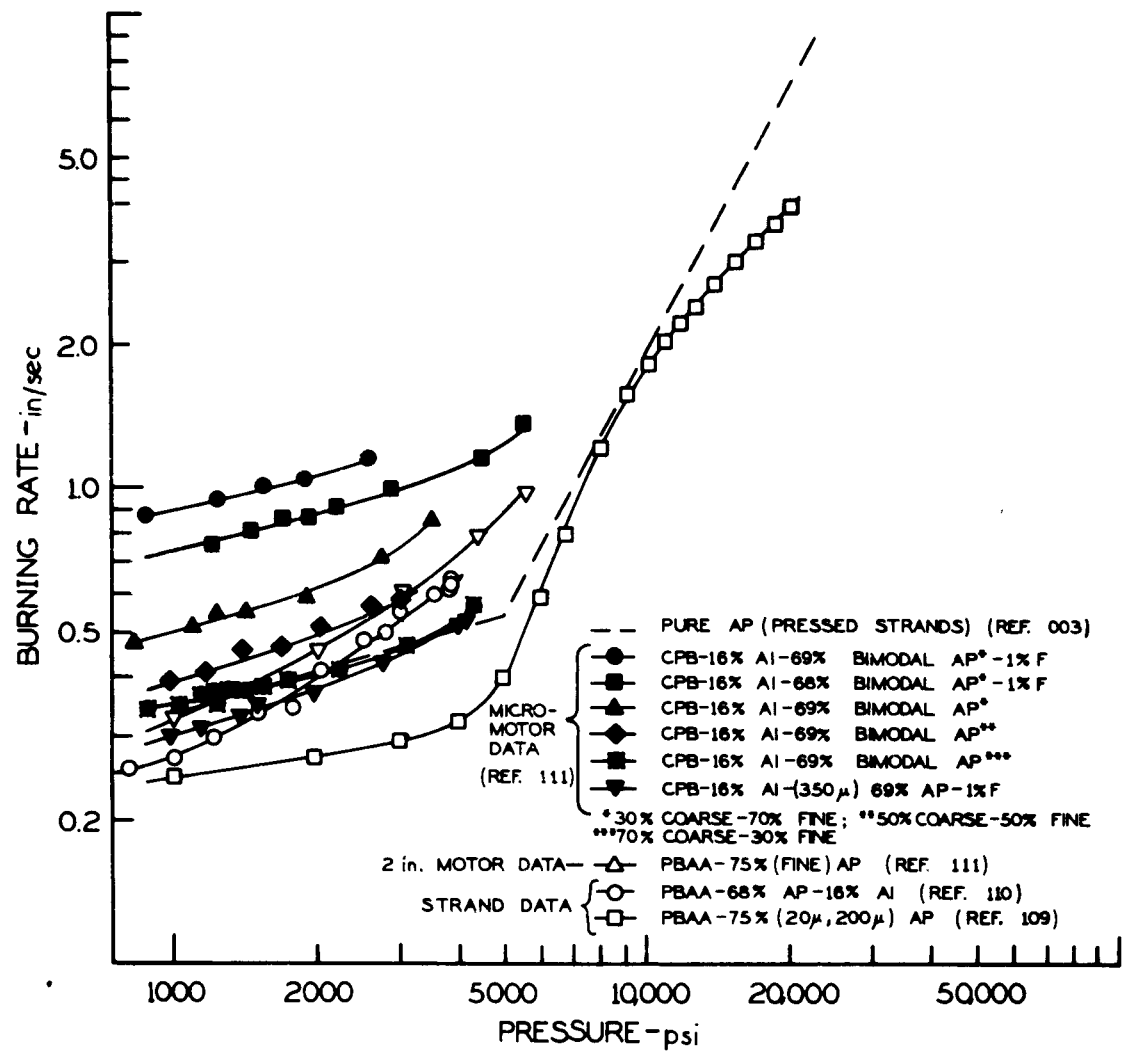


Fig. 7 High pressure r-P data for polybutadiene-NH₄ClO₄ propellants.

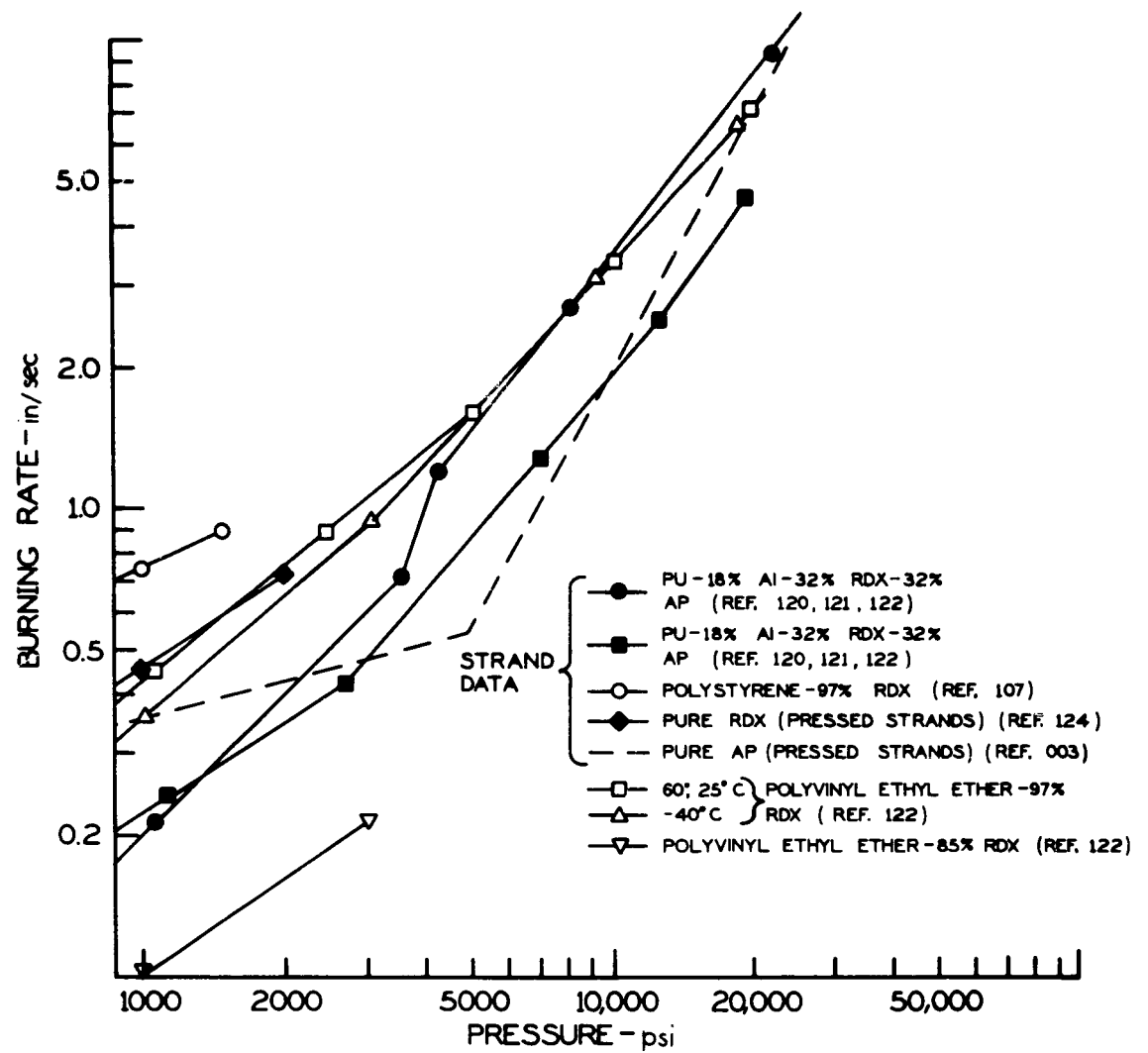


Fig. 8 High pressure r-P data for polyurethane-NH₄ClO₄ propellants containing RDX.

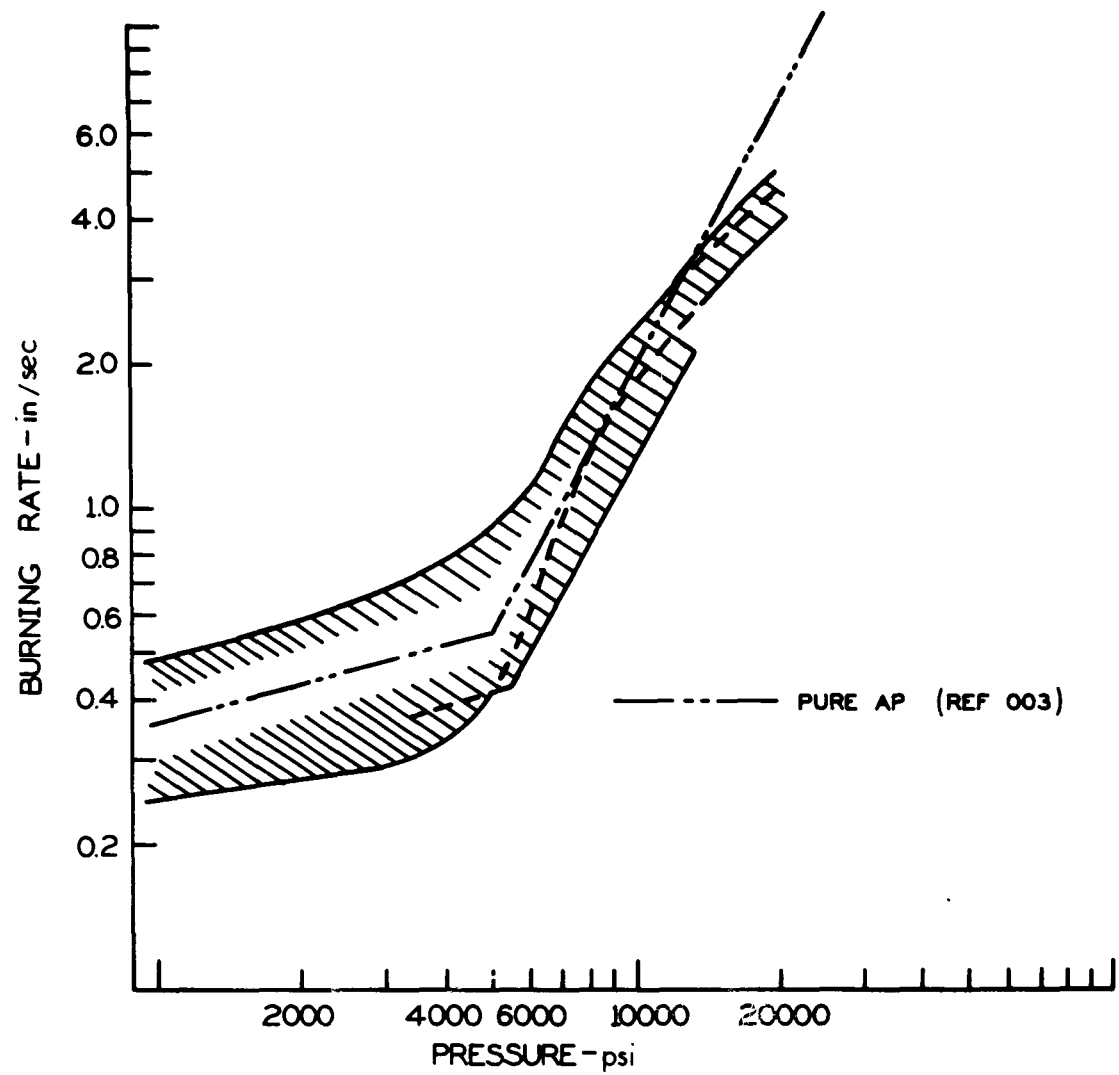


Fig. 9 r-P envelope of inert-binder NH_4ClO_4 propellants studied over a broad pressure range and exhibiting transition.

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